

Adsorbate Infrared Spectral Response Following Femtosecond Metal-Substrate Heating

A.G. Yodh¹, J.P. Culver¹, M. Li², L.G. Jahn^{1,2}, and R.M. Hochstrasser²

¹Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, USA

²Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, USA

Ultrafast laser heating pulses create unique environments for surface chemistry on metal surfaces. Recent femtosecond experiments have shown, for example, that nonequilibrium substrate conditions can play a central role in laser induced desorption[1]. In these experiments extremely high electronic temperatures (4000 °K) are produced which modify adsorbates in a manner which is impossible to achieve via conventional thermal processes. Here we report the experiments probing the internal vibrations of CO adsorbate molecules as a function of time following the impulsive excitation of electrons in the underlying Cu(111) substrate by 300 fs visible light pulses[2]. We find that a low frequency CO mode couples to substrate electrons and phonons, and that the representative coupling rates can be separately determined[2,3]. Importantly, with increased excitation of the substrate, our measurements provide indication of stronger, temperature dependent couplings between the adsorbate vibrations and the substrate reservoirs[4].

Our experiment uses gated upconversion to follow the time evolution of the CO internal stretch vibration ($\omega_o = 2073.5 \text{ cm}^{-1}$, $\Gamma_o = 4.5 \text{ cm}^{-1}$) after femtosecond pulsed heating of the substrate. The metal substrate excitation is described by electron and lattice temperatures, T_e and T_l , having distinctly different temporal profiles (Fig. 1). Although the stretch mode is nominally populated through interaction with these substrate reservoirs, the dominant spectral change is a result of a temperature dependent shift of the oscillator complex frequency. The stretch mode is anharmonically coupled to the frustrated translation mode of the CO complex. As the frustrated translation mode is heated by the excited substrate, the stretch frequency absorption, broadens, and shifts to lower frequency. By measuring the reflectivity on the high frequency side of the CO stretch absorption at 2075 cm^{-1} , the time evolution of the low frequency mode population can be discerned (Fig. 2).

The change in temperature of the low frequency mode can be predicted using a rate equation with independent couplings to the electron (γ_e) and to the phonon (γ_l) reservoirs.

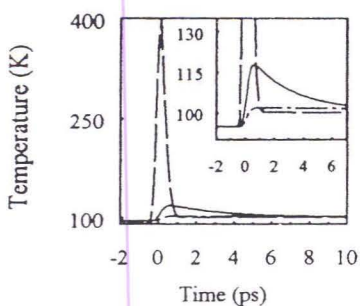


Fig. 1: Calculations of electron and phonon reservoir temperature as a function of time: electronic (dashed line), phonon (dotted dashed line); Adsorbate temperature (solid line) calculated using the best fit values of $\gamma_e = 167(24) \text{ GHz}$ and $\gamma_l = 145(56) \text{ GHz}$. Inset: same with expanded scale.

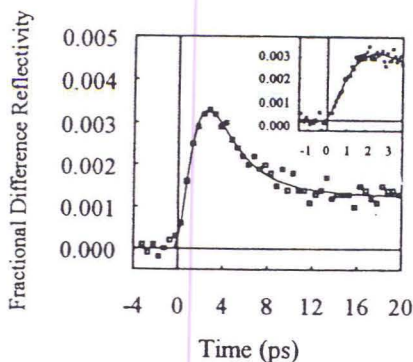


Fig. 2: $F_{abs} = 0.09 \text{ mJ/cm}^2$: Data (open squares), a best fit (solid line) using the model and values described in the text. Inset: rise of the signal.

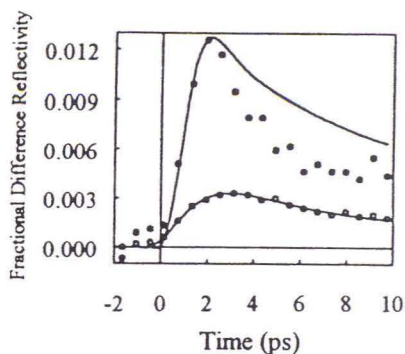


Fig. 3: $F_{abs} = 0.77 \text{ mJ/cm}^2$ (solid circles): $F_{abs} = 0.09 \text{ mJ/cm}^2$ (open circles). The lines represent fits using $\gamma_e = 167 \text{ GHz}$ and $\gamma_l = 145 \text{ GHz}$.

The time evolution of the spectra was calculated using temperature dependent FTIR spectra to predict the corresponding changes in the stretch mode complex frequency. A best fit gives coupling rates $\gamma_e = 167(24) \text{ GHz}$ and $\gamma_l = 145(56) \text{ GHz}$. Couplings to both reservoirs are revealed to be necessary and as a result of relatively large differences in their respective temporal profiles, their respective contributions can be distinguished.

Experiments with eight times greater excitation of the substrate (Fig. 3) exhibit deviations from this model. As the molecule approaches excitation levels near the desorption threshold there are several mechanisms by which energy may be more quickly exchanged with the substrate. These new mechanisms, which include other anharmonic couplings between the adsorbate-like modes, temperature dependencies of γ_e and γ_l , and combined electron-lattice effects, have been discussed in recent molecular dynamics calculations for CO on Cu(100)[4]. Preliminary analysis of the data in Fig. 3 suggests that the deviations maybe indicative of such temperature dependent adsorbate-substrate coupling rates.

References

- [1] R. R. Cavanaugh, D. S. King, J. C. Stephenson and T. F. Heinz, *J. Phys. Chem.* **97**, 786 (1993) and references therein.
- [2] J. P. Culver, M. Li, L. G. Jahn, R.M. Hochstrasser, and A.G. Yodh, *Chem. Phys. Lett.* **214**, 431 (1993).
- [3] T. A. Germer, J. C. Stephenson, E. J. Heilweil and R. R. Cavanaugh, *Phys. Rev. Lett.* **71**, 3327 (1993).
- [4] J. C. Tully, M. Gomez and M. Head-Gordon, *J. Vac. Sci. Technol.* **A11**, 1914 (1993).